

JOINT SYMPOSIUM ON OIL SHALE, TAR SANDS, AND RELATED MATERIAL  
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MODIFIED FISCHER ASSAY  
EQUIPMENT, PROCEDURES AND PRODUCT BALANCE DETERMINATIONS

By

L. Goodfellow, C. E. Haberman and M. T. Atwood  
The Oil Shale Corporation, 1700 Broadway, Denver, Colorado 80202

INTRODUCTION

Fischer assay is a procedure for determining the yield of oil from oil shale or similar material by programmed pyrolysis and collection of products. The major use of the procedure has been in establishing the values of shale properties.

There are many versions of the assay method. The original work on the adaptation of the Fischer retort to oil shale assay was reported in 1949 by K. E. Stanfield and I. C. Frost (Report of Investigation 4477). The routine procedure used by the Bureau of Mines in Laramie involves simultaneous, automated operation of twelve retorts and gives produced oil and water yields but does not measure the evolved gas (1). A procedure for determining product balances was published by the same author (2), which provided for collection and weighing of the product gas, while collecting the produced oil and water as usual. Product gas analyses were reported. A similar procedure was published by J. Ward Smith (3), along with data from very careful, complete material balance studies. Data from replicate runs were examined statistically.

The Fischer assay apparatus in use at The Oil Shale Corporation permits collection of oil and water in the usual manner and allows for gas collection in either an inverted graduated cylinder for simple volume measurement or in an evacuated gas receiver for both volume measurement and analysis by gas chromatography. The equipment was developed primarily for use in support of the 1000 ton per day Parachute Creek semi-works retorting facility, operated by TOSCO, rather than for core analysis. We have investigated the effects of shale particle size and terminal retorting temperature on oil yield and have carried out detailed studies on balances for total material and for carbon, nitrogen and sulfur.

EXPERIMENTAL

Sample Preparation

A basic requirement of good Fischer assay is to start with a sample of shale which is completely representative of the material being investigated. This is best accomplished by reducing the material to fine mesh size and thoroughly blending.

The size of sample required for a specific ore size can be determined by using directions prepared by A. F. Taggart (4). The selected quantity of shale is prepared as follows:

1. If the sample size is large, grind it in a "Jaw-crusher" or "Chipmunk" crusher to minus 1/2-inch size.
2. Stage grind the minus 1/2-inch material to a nominal minus eight mesh using a "coffee-mill" grinder. Each grinding stage should lead to a finer grind, with the minus eight mesh material screened out and only the remaining plus eight mesh material recharged to the mill. Grinding in one stage can result in overheating the sample.
3. Blend the sample using a pad blender and normal blending techniques.
4. Split the blended sample on a Jones Riffle to approximately one gallon.
5. Grind, using an appropriate pulverizer, to minus 65 mesh. (We have found the 6-inch Raymond Mill produced by Combustion Engineering to be satisfactory.)
6. Blend the pulverized sample and split out needed samples on a Jones Riffle.
7. Dry the sample to constant weight at room temperature. Overheating the sample in a drying oven will result in reduced oil yield.

### Operation of Equipment

The apparatus is described in Figure 1. One hundred (100) grams of dried oil shale are placed in a 7-ounce aluminum can which is then placed in the retort, and the retort head is bolted in place using an aluminum gasket for sealing. The charged and sealed autoclave is placed in the Transite heater case equipped with electric heating elements, and the glassware is attached as indicated. The calibrated centrifuge (receiver) tube is immersed in ice water, and ice water is also pumped through the water condenser. The apparatus is checked for leaks by placing under vacuum and observing any changes in an attached vacuum gage. The system is then purged with nitrogen.

Stopcocks are arranged so that the produced gas goes either to the inverted graduated cylinder for routine assay or to the glass gas bomb for complete material balance assay. In the latter case, the mercury switch manometer is set to open the solenoid valve whenever the system pressure exceeds ambient pressure. The opening of the solenoid valve allows gas to flow into the evacuated gas bomb until the system pressure is below ambient, at which time the mercury switch is activated and the solenoid valve is closed.

The heating schedule (below) is started and maintained by manual control of a Variac which feeds power to the electric heating elements in the retort heater case.

<u>Time, minutes</u>	<u>Temperature (°F)</u>
5	113
10	212
15	311
20	419
25	536
30	662
35	761
40	860
45	914
50	932
50 - 70	932
off	

At the end of the heating cycle a nitrogen purge is conducted. If the product gas has been directed into the inverted graduated cylinder the two liquid levels are equalized and the volume reading taken before purging. Nitrogen is then passed through the gas heater and through the retort to force oil remaining on the retort side arm down into the oil receiver. If the evacuated glass gas bomb was used, the hot nitrogen purge is directed similarly through the retort and finally into the gas bomb. From the total volume of the gas bomb and the gas chromatography analysis of the contained gas, the nitrogen contribution can be ascertained and the true product gas quantity determined. As stated below, we have found that nitrogen is not a product of oil shale retorting.

The glass adapter and oil receiver, previously tared, are removed from the retort and water condenser and weighed. The weight increase represents water plus oil. The oil receiver is then separated from the adapter and warmed and centrifuged. The water layer is removed in a tared syringe and weighed, allowing calculation of the weight of oil. The specific gravity of the oil is determined, and the oil and water yields are calculated in gallons per ton of shale. The gas yield is also calculated in SCF per ton.

### RESULTS AND DISCUSSION

#### Statistical Analysis of Data

Forty-two (42) Fischer assays were run in routine fashion by the same operator on a single raw shale sample utilizing gas collection in the inverted graduated cylinder. Data obtained are shown in Table I.

When this work was done the water was determined by visual observation of the calibrated centrifuge tube receiver. Since then we have begun removing the centrifuged water layer in a tared syringe and determining the water by weight difference. This improved procedure should reduce the uncertainty in water yield and, to a lesser extent, the uncertainty in oil yield.

### Modified Fischer Assay Equipment



TABLE I

Results of Forty-Two Replicate Fischer Assays

	<u>Arithmetic Mean</u>	<u>Mean Deviation</u>	<u>Standard Deviation</u>
Oil Yield (gallons per ton)	33.17	0.237	0.291
Gas Yield (SCF per ton)	1028	33.3	45.6
Water Yield (gallons per ton)	2.82	0.28	0.33

Material and Carbon Balances

A sample of 33 gallon per ton oil shale was used in a complete product balance study. The Fischer assay procedure utilized gas recovery in the large, evacuated gas bomb followed by complete gas chromatography analysis. The normalized gas analysis is shown in Table II

TABLE II

Fischer Assay Gas Analysis

<u>Component</u>	<u>Mole %</u>
Hydrogen	36.4
Carbon Monoxide	3.6
Carbon Dioxide	18.0
Hydrogen Sulfide	2.9
Methane	17.2
Ethane	7.1
Ethylene	3.3
Propane	3.2
Propylene	2.9
iso Butane	0.1
n-Butane	1.0
Butenes	1.7
C <sub>5</sub> 's*	1.4
C <sub>6</sub> 's*	0.7
C <sub>7</sub> 's*	0.3
C <sub>8</sub> 's*	0.1
C <sub>9</sub> and heavier	<u>nil</u>
Total	99.9

\* Assumed molecular weight is calculated as  $C_n H (2n + 1)$ .

The raw shale and spent shale were analysed for total carbon by the conventional combustion procedure (5). Inorganic carbon was determined by measuring carbon dioxide released by reaction with hydrochloric acid (6). In raw shale and spent shale the organic carbon value is the difference between total carbon and mineral carbon. Total carbon in the gas was calculated from the total amount of gas and from the analysis shown in Table II. The mineral carbon in the gas was calculated from the difference in mineral carbon values between the raw shale and spent shale, assuming this difference was represented by a portion of the carbon dioxide in the gas (Table I). The remainder of the carbon dioxide in the gas is assumed to be of organic origin. We have found in normal Fischer assay that somewhat more than half of the carbon dioxide in the gas is derived from pyrolysis of inorganic carbonates. J. Ward Smith (3) found in eight replicate runs, with 26 gallon per ton shale, that an average of 50% of the carbon dioxide in the gas was inorganic derived.

The total product balance and total carbon balance are shown in Table III. The organic and inorganic carbon balances are given in Table IV. The contribution of retort water contents to the carbon balances is very small and can be ignored.

It would be straightforward to obtain a hydrogen balance around Fischer assay, but the value of the information would be questionable. There is no reasonable way to distinguish organic hydrogen from hydrogen present as water in the mineral matrix.

Nitrogen and Sulfur Balances

The same raw shale as used above was subjected to additional total product balance

TABLE III

## Product Balances\*

Material	Total Product		Total Carbon	
	Weight (lbs) In	Weight (lbs) Out	Weight (lbs) In	Weight (lbs) Out
Raw Shale	2000		430	
Spent Shale		1648		177.2
Oil		252		213.4
Gas		70.5		38.4
Water		23		---
Total	2000	1993.5	430	429
% Deviation		0.32		0.23

\* Based on one ton of raw shale, 33 gallons per ton Fischer assay oil yield.

TABLE IV

## Organic and Inorganic Carbon Balances\*

Material	Weight(lbs)	Wt. % Organic Carbon	Organic Carbon		Wt. % Inorganic Carbon	Inorganic Carbon	
			Weight(lbs) In	Weight(lbs) Out		Weight(lbs) In	Weight(lbs) Out
Raw Shale	2000	16.43	330.6		4.97	99.40	
Spent Shale	1648	4.94		81.4	5.81		95.75
Oil	252	84.69		213.4	---		---
Gas	70.5	49.25		34.7	5.24		3.69
Water	23	---		---	---		---
Total			330.6	329.4		99.40	99.44
% Deviation				0.36			0.04

\* Based on one ton of raw shale, 33 gallons per ton Fischer assay oil yield.

TABLE V

## Sulfur Balance\*

Material	Weight (lbs)	Wt. % Sulfur	Sulfur	
			Weight (lbs) In	Weight (lbs) Out
Raw Shale	2000	0.75	15	
Spent Shale	1656	0.63		10.4
Oil	250	0.88		2.2
Gas	52	5.42		2.8
Water	22	0.03		nil
Total			15	15.4
% Deviation				2.7

\* Based on one ton of raw shale, 33 gallons per ton Fischer assay oil yield.

TABLE VI

Nitrogen Balance \*

<u>Material</u>	<u>Weight (lbs)</u>	<u>Wt.% N (as NH<sub>3</sub>)</u>	<u>Weight (lbs) In</u>	<u>Weight (lbs) Out</u>
Raw Shale	2000	0.56	11.20	
Spent Shale	1648	0.34		5.60
Oil	252.8	2.21		5.59
Gas				nil
Water	23.0	1.87		<u>0.43</u>
Total			<u>11.20</u>	<u>11.62</u>
% Deviation				3.8

\* Based on one ton of raw shale, 33 gallons per ton Fischer assay oil yield.

TABLE VII

Screen Size vs. Oil Yield

<u>Screen Size (U.S. Standard)</u>	<u>Wt.%</u>	<u>Oil Yield (gallons per ton)</u>	<u>Size Wt.% X Oil Yield</u>
+10	78.6	38.3	30.1
-10 to +20	11.9	35.7	4.2
-20 to +40	4.7	34.1	1.6
-40 to +80	2.6	32.5	0.8
-80	2.2	32.7	0.7
Head Assay*	100	37.2	37.2

Yield by Head Assay\* 37.2 gallons per ton

Yield by Fraction Assay 37.4 gallons per ton

Variance 0.5%

\*Oil yield of undivided, original sample.

TABLE VIII

Effect of Terminal Temperature on Product Yield

(Raw Shale Sample 01-1132)

<u>Terminal (maximum) Temperature (°F)</u>	<u>Oil Yield (gallons per ton)</u>	<u>Water Yield (gallons per ton)</u>	<u>Gas Yield (SCF per ton)</u>
875	35.1	2.4	810
875	35.6	2.4	835
900	37.4	2.9	940
900	37.9	2.9	925
932	38.0	2.8	1260
932	37.9	2.4	1360
932	37.4	2.9	1260
932	37.2	2.2	1330
932	37.7	3.0	1165

Fischer assays, and the charge materials and products were analyzed for nitrogen and sulfur. The nitrogen contents of the raw shale, spent shale, water and oil were determined by conventional Kjeldahl analysis. The sulfur contents of raw shale and spent shale were determined by combustion in a Leco furnace. The sulfur content of the gas was calculated from the hydrogen sulfide content, as determined by gas chromatography. The oil was analyzed for sulfur by X-ray fluorescence. Sulfur in water was assumed to be sulfide and was determined by iodimetric titration.

The amount of nitrogen remaining in the spent shale was unexpected since inorganic nitrogen compounds have not been reported in Green River formation oil shale.

Ammonia is never found in gas produced by shale retorting because of its rapid reaction with both carbon dioxide and hydrogen sulfide in the vapor phase. It is believed that all of the produced ammonia ends up in the retort water.

Independent tests on Fischer assay equipment and at the Parachute Creek semi-works facility, operated by TOSCO, have shown that molecular nitrogen is not a product of shale retorting.

#### Effect of Shale Particle Size on Oil Yield

A sample of crushed shale of random particle size distribution was separated into various screen fractions, and the individual fractions were subjected to the usual sample preparation and Fischer assay. The results are given in Table VII.

The general decrease in oil yield with decreasing particle size is evident. This trend was observed in every case which we investigated.

#### Variation of Product Yields with Terminal Retorting Temperature

The standard retorting time-temperature schedule is described above in the experimental section. It calls for leveling off the retorting temperature at 932°F (500°C) after 50 minutes, maintaining this temperature for an additional 20 minutes and then shutting off power. A brief investigation was made of the effect of varying the terminal temperature on product yield distribution. In each case the time cycle was unchanged, but the maximum temperature was leveled off as soon as it was reached. Data are given in Table VIII.

The 875°F temperature does not permit complete retorting of the oil. There seems to be little difference in oil yield between the two higher temperatures. The difference in gas yields between the two higher temperatures is likely due to formation of more carbon dioxide from inorganic components at the 932°F temperature.

#### LITERATURE CITED

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